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Structural characteristic and magnetic properties of Mn oxide films grown by plasma-assisted MBE

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Abstract

We report on the structural characteristics and magnetic properties of Mn oxide films grown on MgO (0 0 1) substrates by plasma-assisted molecular beam epitaxy (MBE). Under well-controlled growth conditions, three types of Mn oxide films were obtained. They are Mn_3O_4, λ-MnO_2 and their mixed structure ($Mn_3O_4+\lambda$-MnO_2). A structural phase diagram about the films is depicted as a function of growth rate and substrate temperature. It is found that at lower growth rate, a new phase of Mn oxide λ-MnO_2 was obtained, and two transition temperatures were observed in its magnetization. At a higher growth rate, the Mn_3O_4 film was obtained. Its coercive force and transition temperature were different from its bulk sample. The atomic force microscopy (AFM) images exhibited the surfaces of the three films are composed of pyramids, flat surfaces and truncated-pyramids, respectively.

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1. Introduction

Molecular beam epitaxy (MBE) has been demonstrated to be a powerful heteroepitaxial growth technique for thin films. Since it relies on non-equilibrium thermodynamic processes, it allows the growth of materials in a metastable phase by controlling growth conditions. Fabricating new structures or new materials will widen the field of new materials and agitate the research both in fundamental physics and applications. Manganese (Mn) oxides are of great interest due to their wide applications in electrode and alloy materials [1–3]. Though there exists extensive literature about bulk Mn oxides [1–4], relatively few were reported about features of their respective thin films [5,6], which are of considerable interest because of the effect of size on their structure, morphology and physical properties. Furthermore, if structural phases of the films can be controlled well, it would be possible to fabricate multilayer Mn oxides with different structures and properties, such as ferromagnetic and antiferromagnetic behaviors which have potential applications in magnetic data

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storage and sensor devices [7,8]. The present work is devoted to investigation of growth dynamics of Mn oxide films grown by plasma-assisted MBE. Under well-controlled conditions, three types of Mn oxide films were fabricated. Especially, a new structural phase of λ-MnO_2 has been realized. This is the first report on chemical pure λ-MnO_2 films.

Mn oxides crystallize in several different structures with varied proportions of Mn ions (Mn^{2+}, Mn^{3+}, and Mn^{4+}). The stable and well-known Mn oxides are MnO, Mn_3O_4, Mn_2O_3 and MnO_2. Their magnetic, transport and optical properties are closely related to their structures, crystalline quality and stoichiometry [9]. In this paper, three types of Mn oxide films were fabricated on MgO substrates. Their morphology and magnetic properties were studied. A structural phase diagram as function of growth rate and temperature were revealed.

2. Experiments

The Mn oxide films were grown on MgO (0 0 1) substrates at substrate temperature around 550°C–750°C by using a plasma-assisted MBE system. The O_2 pressure was kept at 4×10^{-5} Torr during growth. To characterize the films, X-ray diffraction (XRD) and atomic force microscope (AFM) were used to analyze crystal structure and surface morphology of the films. Their magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

It was found that three types of Mn oxide films were grown depending on growth rates. They are referred to as phase A (Mn_3O_4), phase B ($Mn_3O_4 + \lambda$-MnO_2) and phase C (λ-MnO_2) hereafter.

3.1. Crystal structures

All of these three types of films were well crystallized and possess square symmetry in the growing plane as analyzed by RHEED and XRD. The detailed XRD analysis suggested that the films are (0 0 1) orientated. Phase A is a single crystal Mn_3O_4 film with lattice constants $a = b \approx 5.76$ Å and $c = 9.47$ Å, if a body-centered tetragonal unit-cell is adopted. Phase C is a single crystal λ-MnO_2 film (a new structural phase of Mn oxides) with lattice constant about 8.4 Å (nearly twice that of the MgO substrate), if a face-centered cubic unit cell is adopted. Phase B is a mixed phase consisting of phase A and phase C ($Mn_3O_4 + \lambda$-MnO_2) with the same [0 0 1] orientation.

3.2. Surface morphology

The different Mn oxide films show characteristic surface morphologies as shown in Fig. 1. The surface of the phase A film is shown in Fig. 1(a). It is composed of pyramid-hillocks with well-defined facets {1 0 15} [10]. The surface of the phase C is flat but containing pits. The edges of the pits are zigzagged as shown in Fig. 1(c). The surface of the phase B film is composed of truncated-pyramids as shown in Fig. 1(b), which can be imaged to be formed by cutting the pyramid-hillocks of phase A with a plane from phase C. However, it is necessary to clarify the arrangement of the two mixed phases in the sample of phase B. We note that for all three samples, no matter what phases exist, the base-edge of the (truncated-) pyramid hillocks and the edge of the pits are oriented along the ⟨1 1 0⟩ azimuth of the MgO substrate.

3.3. Structural phase diagram

Analyzing the growth conditions for different phases, a structural phase diagram has been obtained as a function of growth temperature and growth rate under a fixed O_2 pressure as shown in Fig. 2. It can be seen that single crystal Mn_3O_4 films are grown at growth rates above 5 nm/min, while at growth rate below 2 nm/min, phase C is obtained. In between a mixed phase B is observed. The shadow region in Fig. 2 is the transition region where phase C or phase B is obtained depending on the growth temperature. Phase C was favored for higher growth temperatures under the same growth rate. Therefore, the

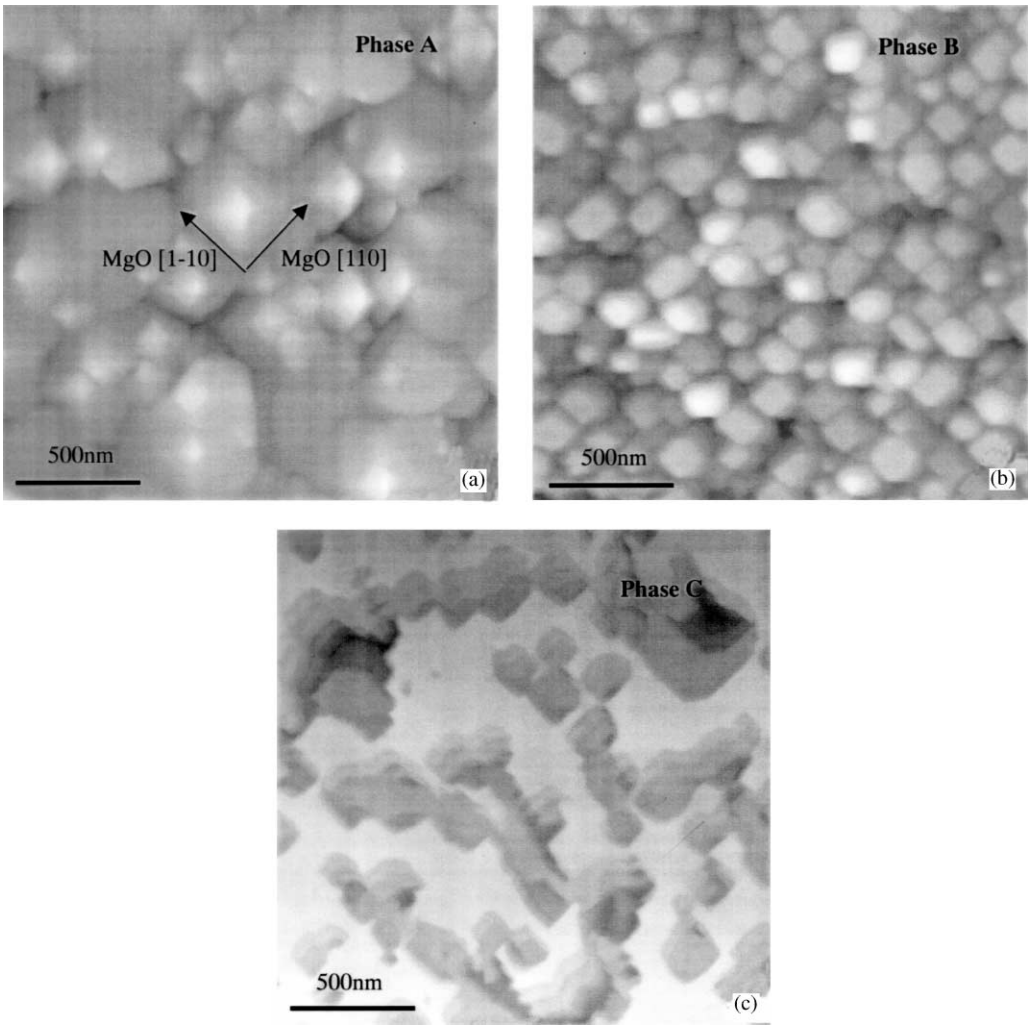

Fig. 1. AFM images of three types of films (a) pyramid-hillocks for phase A, (b) truncated-pyramids for phase B and (c) flat surface with pits for phase C, where pit edges show zigzag structure.

growth rate plays an important role in determining the structural phase, while the growth temperature becomes determinant when the growth rate is within the transition region. However, the XRD analyses indicated that the crystalline quality had a close correlation with growth temperature.

3.4. Magnetic properties

Phase A shows ferrimagnetic long-range order when the temperature is below the Curie temperature (46 K) owing to the exchange interaction of the Mn atoms as shown in Fig. 3(a), which is similar to behavior in corresponding bulk samples. The Curie temperature is slightly higher than the 42 K of the bulk samples due to the slightly reduced lattice constant of the film. Magnetization measurements in the (0 0 1) plane indicated that spontaneous magnetization of the film is about $1.73\,\mu_B$/molecule which is smaller than $1.85\,\mu_B$/molecule of bulk single crystal samples. Its easy axis is along the [1 0 0] or [0 1 0] direction with a

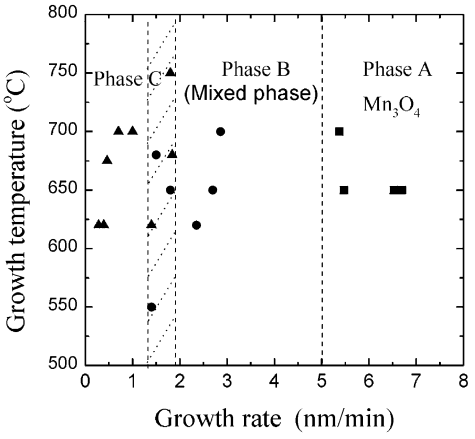

Fig. 2. A structure phase diagram of Mn oxides as functions of growth rate and growth temperature. The filled squares, circles and triangles represent phase A, B and C, respectively. The shadow area is a mixed region for phase B and C, where the phase is determined by the growth temperature.

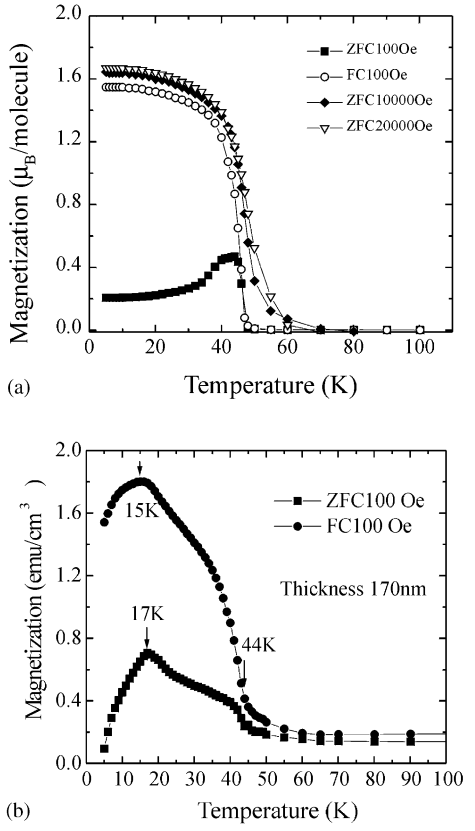

Fig. 3. Dependence of magnetization on temperature for phase A with film thickness 1.4 μm (a) and phase C with film thickness 170 nm (b) under ZFC and FC for different applied field.

coercive force of about 3500 Oe for magnetization reversal measured at 5 K which is larger than the value of 2800 Oe from a bulk single crystal sample [11]. The slightly smaller spontaneous magnetization and larger coercive force observed in the film may be ascribed to strain and film/substrate interface effects.

Magnetization of the phase C was measured under two conditions, field cooled (FC) and zero-field cooled (ZFC) as shown in Fig. 3(b). Two transition temperatures, T_1 and T_2, are observed which was different from bulk polycrystalline samples synthesized by removing Li ions from a parent $LiMn_2O_4$. T_1 is approximate 17 K and corresponds to a long-range antiferromagnetic ordering similar to observation in bulk samples. T_2, about 44 K, is observed for the first time in the λ-MnO_2 film and corresponds to a weak long-range ferromagnetic ordering among the net magnetization of the clusters in which short-range antiferromagnetic ordering was assumed. T_1 shifted to lower temperatures with decreasing thickness of the film which indicated that the interface and strain play a key role in determining the transition temperature.

The magnetic properties of phase B are similar to that of bulk polycrystalline Mn_3O_4 or bulk polycrystalline λ-MnO_2 samples, depending on the ratio of the two compositions. The reason for the behavior of phase B is similar to that of polycrystalline film is presumably due to existing domain interfaces between phases A and C in phase B films.

4. Conclusions

Three types of structural phases of Mn oxide films were obtained. Their surface morphology and magnetic properties are closely correlated with their crystalline structures. λ-MnO_2, a new Mn oxide film, was obtained for the first time and two transition temperatures were observed in the films, which are different from the bulk polycrystalline samples. A structure phase diagram is revealed which is helpful to understand growth dynamics of Mn oxide films.

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